

CLAIMS

1. A method for conducting electroplating in the presence of CO₂ and a metal salt-containing aqueous solution, the CO₂ being liquid, subcritical or supercritical, the method further
5 comprising a step of adding a nonionic compound having a CO₂-affinitive moiety to a system wherein the aqueous solution and CO₂ coexist, the CO₂-affinitive moiety being at least one member selected from the group consisting of:

(1) homopolymers, bicopolymers and tricopolymers of
10 polyoxypropylene, polyoxybutylene and/or polyoxyethylene;

(2) fluorine-containing alkyl groups in which some or all of the hydrogen atoms are substituted by fluorine;

(3) fluorine-containing polyether groups in which some or all of the hydrogen atoms are substituted by fluorine; and

15 (4) dialkylsiloxo groups.

2. The method according to Claim 1, wherein the nonionic compound is an ether-based or ester-based compound.

20 3. The method according to Claim 1, wherein the nonionic compound is an alcohol-based compound.

4. The method according to Claim 1, wherein the nonionic compound is a fluorinated hydrocarbon.
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5. The method according to Claim 1, wherein the nonionic compound is a polyalkylsiloxane.

6. The method according to Claim 1, wherein the
30 nonionic compound is a fluorine-containing polymer.

7. A plating bath comprising a metal salt-containing aqueous solution, CO₂, and a nonionic compound having a CO₂-affinitive moiety, the CO₂ being liquid, subcritical or

supercritical, the CO₂-affinitive moiety being at least one member selected from the group consisting of:

(1) homopolymers, bicopolymers and tricopolymers of polyoxypropylene, polyoxybutylene and/or polyoxyethylene;

5 (2) fluorine-containing alkyl groups in which some or all of the hydrogen atoms are substituted by fluorine;

(3) fluorine-containing polyether groups in which some or all of the hydrogen atoms are substituted by fluorine; and

10 (4) dialkylsiloxo groups.

8. An additive for use in electroplating conducted in the presence of liquid, subcritical or supercritical CO₂, the additive comprising a nonionic compound having a CO₂-affinitive moiety,

15 the CO₂-affinitive moiety being at least one member selected from the group consisting of:

(1) homopolymers, bicopolymers and tricopolymers of polyoxypropylene, polyoxybutylene and/or polyoxyethylene;

20 (2) fluorine-containing alkyl groups in which some or all of the hydrogen atoms are substituted by fluorine;

(3) fluorine-containing polyether groups in which some or all of the hydrogen atoms are substituted by fluorine; and

(4) dialkylsiloxo groups.

25 9. A method for preprocessing conducted before plating comprising the step of degreasing and washing a plating substrate prior to plating using a nonionic compound having a CO₂-affinitive moiety,

30 the CO₂-affinitive moiety being at least one member selected from the group consisting of:

(1) homopolymers, bicopolymers and tricopolymers of polyoxypropylene, polyoxybutylene and/or polyoxyethylene;

(2) fluorine-containing alkyl groups in which some or all of the hydrogen atoms are substituted by fluorine;

35 (3) fluorine-containing polyether groups in which some

or all of the hydrogen atoms are substituted by fluorine; and

(4) dialkylsiloxo groups.

10. A method for postprocessing conducted after plating
5 comprising the step of washing a plated film after plating using
a nonionic compound having a CO₂-affinitive moiety, the CO₂-
affinitive moiety being at least one member selected from the
group consisting of:

(1) homopolymers, bicopolymers and tricopolymers of
10 polyoxypropylene, polyoxybutylene and/or polyoxyethylene;

(2) fluorine-containing alkyl groups in which some or
all of the hydrogen atoms are substituted by fluorine;

(3) fluorine-containing polyether groups in which some
or all of the hydrogen atoms are substituted by fluorine; and

15 (4) dialkylsiloxo groups.

11. A plated film having

(1) per cm², not more than one pinhole having a diameter
of at least 1 μm;

20 (2) a film thickness of not more than 1 μm; and

(3) a plated film surface roughness of not greater than
10 nm.

12. The method according to Claim 1, wherein the
25 nonionic compound used is (CO₂-affinitive moiety)-X- or X-(CO₂-
affinitive moiety)-X- of 1) or 2) below respectively:

1) F-(CF₂)_q-(OCF₃F₆)_m-(OC₂F₄)_n-(OCF₂)_o-(CH₂)_p-X-, or

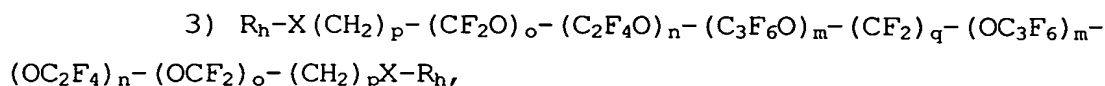
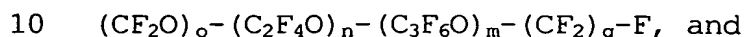
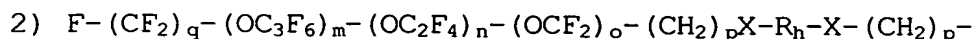
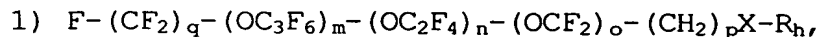
2) -X-(CH₂)_p-(CF₂O)_o-(C₂F₄O)_n-(C₃F₆O)_m-(CF₂)_q-(OC₃F₆)_m-
(OC₂F₄)_n-(OCF₂)_o-(CH₂)_p-X-,

30 wherein m, n, o, p, and q are integers not smaller than
0, m and n are integers from 0 to 15 but not both 0, n + m ≤ 20,
o = 0 to 20, p = 0 to 2, and q = 1 to 10; the sequence of the
repeating units not being fixed; -(OC₃F₆)_m- represents -
(OCF₂CF₂CF₂)_m- or -(OCF(CF₃)CF₂)_m-, and -(OC₂F₄)_n- represents -
35 (OCF₂CF₂)_n- or -(OCF(CF₃))_n-, and

each X may be the same or different, and represents a single bond, or O, S, NH, NR (R^a : alkyl group), C=O, C(O)O, OC(O), C(O)S, SC(O), C(O)NH, C(O)NR^a (R^a : alkyl group), NH(O)C, NR(O)C, CH₂, CHR^a, CR^a₂ (R^a : alkyl group), SO₂NH, or NHSO₂.

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13. The method according to Claim 1, wherein the nonionic compound is one of 1) to 3):



wherein m, n, o, p, and q are integers not smaller than 0, m and n are integers from 0 to 15 but not both 0, $n + m \leq 20$,
 15 $o = 0$ to 20, $p = 0$ to 2, and $q = 1$ to 10; the sequence of the repeating units not being fixed; $-(\text{OC}_3\text{F}_6)_m-$ represents $-(\text{OCF}_2\text{CF}_2\text{CF}_2)_m-$ or $-(\text{OCF}(\text{CF}_3)\text{CF}_2)_m-$, and $-(\text{OC}_2\text{F}_4)_n-$ represents $-(\text{OCF}_2\text{CF}_2)_n-$ or $-(\text{OCF}(\text{CF}_3))_n-$, and

each X may be the same or different, and represents a
 20 single bond, or O, S, NH, NR (R^a : alkyl group), C=O, C(O)O, OC(O), C(O)S, SC(O), C(O)NH, C(O)NR^a (R^a : alkyl group), NH(O)C, NR(O)C, CH₂, CHR^a, CR^a₂ (R^a : alkyl group), SO₂NH, or NHSO₂, and each R_h is a hydrophilic moiety and a straight or branched chain hydrocarbon group that may contain hetero atoms.

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14. The method according to Claim 13, wherein R_h is a polyoxyalkylene group.

15. The method according to Claim 13, wherein the
 30 nonionic compound comprises a CO₂-affinitive moiety whose number of carbon atoms is the same as or greater than that of the R_h group.

16. The method according to Claim 1, wherein the
 35 nonionic compound comprises (CO₂-affinitive moiety)-X- or X-(CO₂-

affinitive moiety)-X- of 1) or 2) below respectively:

1) $Y-(CF_2)_{m1}-(CH_2)_{n1}-X$, or

2) $X-(CH_2)_{n1}-(CF_2)_{m1}-(CH_2)_{n1}-X$,

wherein Y is F or H, each X may be the same or
5 different and represents one member selected from the group
consisting of COO, O, S, CONH, NHCO, SO₂NH, and NHSO₂, m1 is an
integer from 3 to 20, and each n1 may be the same or different
and represents an integer from 0 to 2.

10 17. The method according to Claim 16, wherein the
nonionic compound is one of 1) to 3) below respectively:

1) $Y-(CF_2)_{m1}-(CH_2)_{n1}-X-R_h$,

2) $Y-(CF_2)_{m1}-(CH_2)_{n1}-X-R_h-X-(CH_2)_{n1}-(CF_2)_{m1}-Y$, or

3) $R_h-X-(CH_2)_{n1}-(CF_2)_{m1}-(CH_2)_{n1}-X-R_h$,

15 wherein Y is F or H, each X may be the same or
different and represents one member selected from the group
consisting of COO, O, S, CONH, NHCO, SO₂NH, and NHSO₂, each m1 may
be the same or different and represents an integer from 3 to 20,
each n1 may be the same or different and represents an integer
20 from 0 to 2, and each R_h is a hydrophilic moiety and straight or
branched chain hydrocarbon group that may contain hetero atoms.

18. The method according to Claim 17, wherein R_h is a
polyoxyalkylene group.

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19. The method according to Claim 17, wherein the
nonionic compound comprises a CO₂-affinitive moiety whose number
of carbon atoms is the same as or greater than that of each R_h
group.

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